

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 685 565 A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art.
158(3) EPC

(21) Application number: **94917168.0**

(51) Int. Cl.⁸: **C22C 5/02**

(22) Date of filing: **07.06.94**

(66) International application number:
PCT/JP94/00920

(67) International publication number:
WO 95/07367 (16.03.95 95/12)

(30) Priority: **06.09.93 JP 245981/93**

(43) Date of publication of application:
06.12.95 Bulletin 95/49

(84) Designated Contracting States:
AT CH DE ES FR GB IT LI

(71) Applicant: **MITSUBISHI MATERIALS CORPORATION**
5-1, Otemachi 1-chome
Chiyoda-ku,
Tokyo 100 (JP)

(72) Inventor: **UCHIYAMA, Naoki Sanda Plant**
Mitsubishi Materials Corporation
12-6 Tekunopahku
Sanda-shi
Hyohgo-ken 669-13 (JP)
Inventor: **ISHII, Toshinori Sanda Plant**
Mitsubishi Materials Corporation
12-6 Tekunopahku
Sanda-shi
Hyohgo-kenn 669-13 (JP)

(74) Representative: **Potte, Willi**
KUHNEN.WACKER & PARTNER
Alols-Steinacker-Str. 22
D-85354 Freising (DE)

EP 0 685 565 A1

(54) **GOLDEN ORNAMENT MATERIAL HARDENED BY ALLOYING WITH MINOR COMPONENTS.**

(57) A golden ornament material hardened by alloying pure gold having a purity of 99 % or above with 200-2000 ppm of one or more elements selected from Ca, Ba, Ge and B, and, when necessary, 10-500 ppm of one or more elements selected from Mg, Al, Si, Mn, Fe, Co, Ni, Cu, Pd, Ag, In, Sn, Sb, Pb and Bi and/or 10-1000 ppm of one or more rare earth elements including Y based on the total quantity of the resultant mixture.

TECHNICAL FIELD

The present invention relates to gold materials for accessories which are damaged little by rubbing or scratching, as being highly hard to have a Vickers hardness (Hv) of 100 or more, and which maintain said high hardness independently of time or even after heated by brazing or the like.

BACKGROUND ART

Heretofore, in general, Au alloys having an elevated Hv of 100 or more have been popularly used to produce accessories such as neck chains, brooches, rings, etc. Such Au alloys include, for example, K14 alloys and K18 alloys comprising pure gold having a purity of 99 % or more and approximately from 25 to 40 % by weight of alloying components such as Ag, Cu and even Ni, Pd, Zn, etc.

On the other hand, it is said ideal that the above-mentioned accessories are made of pure gold in view of their color and high-quality appearance. However, pure gold has Hv of about 32 as its ingot, while having Hv of about 80 as its worked wire. Even though such pure gold is worked to have an elevated hardness, the elevated hardness of the thus-worked pure gold is inevitably lowered not only with the lapse of time but also when heated by brazing or the like. For these reasons, pure gold accessories are always soft and are therefore easily scratched. It is extremely difficult to keep the esthetic value of such pure gold accessories for a long period of time, and the practical application of pure gold accessories is limited to only an extremely narrow range at present.

DESCRIPTION OF THE INVENTION

We, the present inventors have studied, from the above-mentioned viewpoints, so as to elevate the hardness of pure gold accessories without detracting from their high esthetic value mentioned above and, as a result, have found that:

when pure gold having a purity of 99 % or more is alloyed with from 200 to 2000 ppm, preferably from 800 to 1800 ppm, more preferably from 1000 to 1600 ppm, relative to the total weight of the resulting gold alloy, of one or more alloying components selected from Ca, Be, Ge and B, then the resulting gold alloy can have an elevated Hv of 100 or more, while still maintaining said elevated hardness independently of time or even after heated by brazing or the like, and in addition, since the content of the above-mentioned alloying components is small, the hardened gold alloy can still maintain the color and the high quality of pure gold itself and therefore can be formed into gold accessories capable of maintaining a high esthetic value comparable to that of pure gold accessories for a long period of time, that;

when said pure gold is alloyed with said alloying component(s) and also from 10 to 500 ppm, preferably from 50 to 400 ppm, more preferably from 100 to 300 ppm, relative to the total weight of the resulting gold alloy, of one or more other alloying components selected from Mg, Al, Si, Mn, Fe, Co, Ni, Cu, Pd, Ag, In, Sn, Sb, Pb and Bi, then the resulting gold alloy can have an elevated mechanical strength, and that;

when said pure gold is alloyed with said alloying component(s) and also from 10 to 1000 ppm, preferably from 100 to 500 ppm, more preferably from 200 to 400 ppm, relative to the total weight of the resulting gold alloy, of one or more other alloying components selected from rare earth elements including Y, then the resulting gold alloy can have much more improved plastic workability such as drawing workability and rolling workability.

The present invention has been attained on the basis of the above-mentioned findings and is characterized in that it provides hardened gold materials for accessories comprising:

pure gold having a purity of 99 % or more and from 200 to 2000 ppm, preferably from 800 to 1800 ppm, more preferably from 1000 to 1600 ppm, relative to the total weight of the resulting gold alloy, of one or more alloying components selected from Ca, Be, Ge and B (hereinafter generically referred to as "hardness-improving components"), and optionally,

(a) from 10 to 500 ppm, preferably from 50 to 400 ppm, more preferably from 100 to 300 ppm, relative to the total weight of the resulting gold alloy, of one or more other alloying components selected from Mg, Al, Si, Mn, Fe, Co, Ni, Cu, Pd, Ag, In, Sn, Sb, Pb and Bi (hereinafter generically referred to as "strength-improving components"), and/or

(b) from 10 to 1000 ppm, preferably from 100 to 500 ppm, more preferably from 200 to 400 ppm, relative to the total weight of the resulting gold alloy, of one or more other alloying components selected from rare earth elements including Y (hereinafter referred to as "workability-improving components").

In the present invention, pure gold to be alloyed shall have a purity of 99 % or more. This is because if gold having a purity of less than 99 % is alloyed according to the present invention, the resulting gold alloy

no more has the golden color which pure gold possesses and therefore loses the high-quality appearance of pure gold.

The reason why the content of the hardness-improving component(s) is defined to fall within the range between 200 ppm and 2000 ppm is because, if it is less than 200 ppm, it is impossible to elevate the hardness of the resulting gold alloy to have Hv of 100 or more and is also impossible to prevent the thus-elevated hardness of the gold alloy from being lowered with the lapse of time or when the gold alloy is heated. On the other hand, if said content is more than 2000 ppm, the gold alloy can no more have the color and the high-quality appearance of pure gold itself with the result that the esthetic value of the gold alloy is lowered.

The reason why the content of the strength-improving component(s) and that of the workability-improving component(s) are defined to fall within the range between 10 ppm and 500 ppm and within the range between 10 ppm and 1000 ppm, respectively, is because, if they are less than 10 ppm, it is impossible to attain the intended effects to improve the mechanical strength and the plastic workability of the gold alloy. On the other hand, if they are more than 500 ppm or 1000 ppm, the color of the gold alloy is noticeably worsened.

BEST MODES OF PRACTICING THE INVENTION

Next, the gold materials for accessories of the present invention are described concretely by means of their examples.

Pure gold having a purity shown in Tables 1 to 6 was melted in an ordinary vacuum melting furnace, to which was/were added alloying component(s) of the amount(s) also shown in Tables 1 to 6. Next, the resulting gold alloy was cast into a columnar ingot having a diameter of 20 mm and a length of 100 mm, and test pieces were cut out of the ingot. The hardness (micro-Vickers hardness under 100 gr) of the test piece was measured. The test piece was chamfered and then introduced into a single-head drawing machine where it was repeatedly drawn by 20 passes to be formed into a wire having a diameter of 0.5 mm. In this way, gold alloy wire samples, Nos. 1 to 55 of the present invention were prepared. As a control, a pure gold wire sample was prepared in the same manner as above, except that no alloying component was added.

The hardness (micro-Vickers hardness under 100 gr) of each of these wire samples was measured immediately after having been drawn and after having been stored for 6 months. In addition, each wire sample was, immediately after having been drawn, heated at 450 °C for 30 minutes and then cooled under the conditions corresponding to those for ordinary brazing, for example, using a soldering alloy of Au:3 wt.-%-Si having a melting point of 370 °C or a soldering alloy of Au:12 wt.-%-Ge having a melting point of 350 °C. The hardness of each of the thus heat-treated wire samples was also measured in the same manner as above. In order to evaluate the mechanical strength of each wire sample, the tensile strength of each wire sample was measured immediately after having been drawn. The results obtained are shown in Tables 7 to 10.

Table 1

Samples	Purity of Pure gold (%)	Content(s) of Alloying Component(s)			(s)
		Hardness-improving Component(s)	Strength-improving Component(s)	Workability-improving Component(s)	
1	99.69	Ca: 404	-	-	-
2	99.84	Be: 841	-	-	-
3	99.38	Ge: 865	-	-	-
4	99.85	D: 391	-	-	-
5	99.56	Ca: 573, Be: 798	-	-	-
6	99.35	Be: 68, Ge: 584	-	-	-
7	99.37	Ge: 92, D: 420	-	-	-
8	99.94	Ca: 508, Be: 73, Ge: 376	-	-	-
9	99.67	Be: 876, Ge: 599, D: 504	-	-	-
10	99.39	Ca: 388, Be: 430, Ge: 18, D: 359	-	-	-

Gold Alloy Wire Samples of the Invention for Accessories

Table 2

Samples	Purity of Pure gold (%)	Content(s) of Alloying Component(s)			(ppm)
		Hardness-improving Component(s)	Strength-improving Component(s)	Workability-improving Component(s)	
11	99.61	Ca: 481	-	Y: 699	
12	99.90	Be: 1535	-	La: 615	
13	99.86	Ge: 231	-	Ce: 740	
14	99.45	B: 629	-	Pr: 810	
15	99.95	Ca: 401, Be: 157	-	Nd: 101	
16	99.64	Be: 845, Ge: 770	-	Pm: 20	
17	99.72	Ge: 615, B: 774	-	Sm: 899	
18	99.87	Ca: 298, Ge: 335	-	Eu: 543	
19	99.52	Be: 539, B: 1001	-	Gd: 921	
20	99.40	Ge: 241, B: 56	-	Tb: 559	

Gold Alloy Wire Samples of the Invention for Accessories

Table 3

Samples	Purity of Pure gold (%)	Content(s) of Alloying Component(s)			(ppm)
		Hardness-improving Component(s)	Strength-improving Component(s)	Workability-improving Component(s)	
21	99.43	Ca: 599, Ge: 388, B: 27	-	Dy: 17	
22	99.75	Be: 269	-	Y: 727, La: 29	
23	99.77	Ge: 639	-	La: 195, Ce: 474	
24	99.43	B: 1055	-	Pr: 324, Nd: 19	
25	99.43	Cu: 692	-	Pm: 668, Sm: 83	
26	99.67	Ca: 49, Be: 399	-	Eu: 682, Gd: 49	
27	99.95	Ge: 503, B: 231	-	Y: 219, Tb: 283, Dy: 111	
28	99.44	Be: 469, Ge: 33	-	La: 84, Pr: 578, Pm: 327	
29	99.86	Ge: 899	-	Ku: 224, Gd: 108, Tb: 253	
30	99.73	Be: 579	-	Ce: 58, Pr: 268, Nd: 123, Pm: 59	

Gold Alloy Wire Samples of the Invention for Accessories

Table 4

Samples	Purity of Pure gold (%)	Content(s) of Alloying Component(s)			(12)
		Hardness-improving Component(s)	Strength-improving Component(s)	Workability-improving Component(s)	
31	99.34	Ca: 776	Mg: 225	-	-
32	99.54	Be: 212	Al: 273	-	-
33	99.52	Ge: 619	Si: 197	-	-
34	99.46	B: 918	Mn: 241	-	-
35	99.65	Ca: 582, Be: 18	Fe: 66	-	-
36	99.37	Ge: 180, B: 360	Co: 91	-	-
37	99.83	Ca: 199, Be: 203, Ge: 15	Ni: 247	-	-
38	99.46	Ca: 84, Be: 51, Ge: 910, B: 483	Cu: 220	-	-
39	99.57	Ca: 934	Pd: 196	Y: 102	-
40	99.92	De: 890	Ag: 62	Ce: 620	-

Gold Alloy Wire Samples of the Invention for Accessories

Table 5

Samples	Purity of Pure gold (%)	Content(s) of Alloying Component(s)			(ppm)
		Hardness-improving Component(s)	Strength-improving Component(s)	Workability-improving Component(s)	
41	99.97	Ce:704	In:181	Nd:989	
42	99.44	B:959	Sn:308	Sm:237	
43	99.83	Ca:876, Ce:890	Sb:148	Cd:731	
44	99.87	Be:513, B:895	Pb:97	Dy:402	
45	99.91	Be:157, Ce:608	Bi:231	Y:389, Ce:520	
46	99.85	Ca:527	Mg:237, Al:121	Pr:394	
47	99.84	Be:584	Si:253, Mn:11	Nd:587, Sm:105	
48	99.90	Ce:1289	Fe:47, Co:284	Pr:432, Pm:210, Gd:13	

Gold Alloy Wire Samples of the Invention for Accessories

Table 6

Samples	Purity of Pure gold (%)	Content(s) of Alloying Component(s)			(1a)
		Hardness-improving Component(s)	Strength-improving Component(s)	Workability-improving Component(s)	
Gold Alloy Wire Samples of the Invention for Accessories	49 99. 91	B: 489	Ni: 67, Cu: 181	La: 56, Nd: 99, Eu: 123, Tb: 59	
	50 99. 86	Ca: 235, B: 52	Pd: 29, Ag: 144, In: 69	Ce: 144, Pm: 6, Gd: 19	
	51 99. 58	Ca: 452, Ge: 326	Sn: 222, Sb: 117, Pb: 26	Pr: 45, Eu: 399	
	52 99. 91	Be: 669, B: 268	Co: 188, Ag: 59, Bi: 263	Nd: 33	
	53 99. 53	Ca: 456, Ge: 364	Al: 165, Mn: 26, Co: 79, Cu: 110	Ce: 59, Sm: 628	
Pure Gold Wire Sample for Accessories	54 99. 40	Be: 1698	Ni: 120, Pd: 33, In: 56, Sn: 139	Dy: 23	
	55 99. 72	Ca: 523, Ge: 098	Mg: 87, Si: 59, Fe: 129, Cu: 44, Ag: 168	Ce: 19	
	99. 99	-	-	-	-

Table 7

Samples	Hardness (H v)				Tensile Strength (kg/mm ²)
	Ingot	Immediately After Being Drawn	After Being Stored for 6 Months	Immediately After Being Heated	
Gold Alloy Wire Samples of the Invention for Accessories	1	53	105	104	37.7
	2	59	110	109	41.9
	3	57	109	108	39.2
	4	51	104	104	37.8
	5	62	119	119	41.8
	6	61	117	117	40.8
	7	58	109	109	40.0
	8	63	121	120	42.6
	9	66	123	123	47.7
	10	63	121	121	45.8
	11	69	137	137	46.2
	12	73	141	141	48.9
	13	68	128	128	47.1
	14	62	120	120	42.9

Table 8

Samples		Hardness (H v)				Tensile Strength (kg/mm ²)
		Ingot	Immediately After Being Drawn	After Being Stored for 6 Months	Immediately After Being Heated	
Gold Alloy Wire Samples of the Invention for Accessories	15	57	113	113	112	41.7
	16	64	128	128	125	48.8
	17	72	141	141	138	49.9
	18	66	124	124	122	48.6
	19	71	143	143	142	51.2
	20	57	115	115	113	44.3
	21	65	131	131	128	43.8
	22	65	132	132	127	46.7
	23	58	114	114	112	44.8
	24	62	123	122	123	49.0
	25	55	111	111	111	42.5
	26	59	119	119	115	45.8
	27	63	123	123	122	46.8
28	68	131	131	128	49.3	

Table 9

Samples	Hardness (H v)				Tensile Strength (kg/mm^2)
	Ingot	Immediately After Being Drawn	After Being Stored for 6 Months	Immediately After Being Heated	
Gold Alloy Wire Samples of the Invention for Accessories	29	65	130	130	50.3
	30	53	125	123	47.6
	31	65	126	124	52.3
	32	67	135	134	54.8
	33	59	112	110	53.5
	34	59	118	115	53.2
	35	62	121	120	53.8
	36	66	131	129	53.1
	37	59	119	118	52.8
	38	56	131	128	55.8
	39	64	129	127	55.7
	40	66	131	127	55.4
	41	62	129	127	61.3
	42	60	121	119	56.8

Table 10

5

10

15

20

25

30

35

40

45

50

Samples	Hardness (Hv)				Tensile Strength (kg/mm ²)
	Ingot	Immediately After Being Drawn	After Being Stored for 6 Months	Immediately After Being Heated	
Gold Alloy Wire Samples of the Invention for Accessories	43	75	143	143	62.5
	44	68	139	137	58.3
	45	61	126	124	52.7
	46	66	129	127	53.8
	47	63	130	128	55.6
	48	72	140	138	56.9
	49	59	123	121	54.8
	50	61	123	120	58.8
	51	64	131	130	59.3
	52	61	124	123	60.1
	53	63	127	125	57.7
	54	75	142	142	62.3
	55	62	127	127	60.4
Pure Gold Wire Sample for Accessories	32	80	35	30	31.6

From the results shown in Tables 1 to 10, it is known that all the gold alloy wire samples of the present invention, Nos. 1 to 55 always had a high hardness, namely, Hv of 100 or more even after being stored or even after being heated, while the hardness of the pure gold wire sample having Hv of less than 100 was noticeably lowered after being stored and after being heated. It is therefore obvious that the stability of the hardness of the gold alloy wire samples of the present invention is significantly higher than that of the pure gold wire sample and that the mechanical strength of the former containing strength-improving component-

(s) was extremely improved.

As mentioned hereinabove, the gold materials for accessories of the present invention are hardly scratched as stably and always having an elevated Hv of 100 or more even after being stored or heated. Moreover, since the content of the alloying components in the gold materials of the present invention is small, the gold materials have, in addition to said high hardness, an esthetic value comparable to the excellent esthetic value of pure gold and maintain said esthetic value for a long period of time due to their high hardness. The gold materials for accessories of the present invention thus have practically useful characteristics.

10 Claims

1. A hardened gold material for accessories comprising;
pure gold having a purity of 99 % or more and from 200 to 2000 ppm, relative to the total weight of the resulting gold alloy, of one or more alloying components selected from Ca, Be, Ge and B.
- 15 2. A hardened gold material for accessories comprising;
pure gold having a purity of 99 % or more, from 200 to 2000 ppm, relative to the total weight of the resulting gold alloy, of one or more alloying components selected from Ca, Be, Ge and B, and from 10 to 500 ppm, relative to the same, of one or more other alloying components selected from Mg, Al, Si,
20 Mn, Fe, Co, Ni, Cu, Pd, Ag, In, Sn, Sb, Pb and Bi.
3. A hardened gold material for accessories comprising;
pure gold having a purity of 99 % or more, from 200 to 2000 ppm, relative to the total weight of the resulting gold alloy, of one or more alloying components selected from Ca, Be, Ge and B, and from 10
25 to 1000 ppm, relative to the same, of one or more other alloying components selected from rare earth elements including Y.
4. A hardened gold material for accessories comprising;
pure gold having a purity of 99 % or more, from 200 to 2000 ppm, relative to the total weight of the
30 resulting gold alloy, of one or more alloying components selected from Ca, Be, Ge and B, from 10 to 500 ppm, relative to the same, of one or more other alloying components selected from Mg, Al, Si, Mn, Fe, Co, Ni, Cu, Pd, Ag, In, Sn, Sb, Pb and Bi, and from 10 to 1000 ppm, relative to the same, of one or more other alloying components selected from rare earth elements including Y.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP94/00920

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl⁵ C22C5/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl⁵ C22C5/00-5/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, A, 62-290836 (Tanaka Denshi Kogyo K.K.), December 17, 1987 (17. 12. 87), Lines 5 to 8, left column, page 1 and lines 7 to 8, upper right column, page 2, (Family: none)	1
X	JP, A, 2-170931 (Mitsubishi Metal Corp.), July 2, 1990 (02. 07. 90), Lines 5 to 16, left column, page 1, (Family: none)	1-4
X	JP, A, 1-87734 (Tanaka Kinzoku Kogyo K.K.), March 31, 1989 (31. 03. 89), Lines 5 to 8, left column, page 1 and lines 6 to 11, lower right column 1, page 2, (Family: none)	1-4
P	JP, A, 6-179931 (Mitsubishi Materials Corp.), June 28, 1994 (28. 06. 94), Lines 2 to 7, left column, page 2, (Family: none)	2

☒ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"Z" document member of the same patent family

Date of the actual completion of the international search

August 30, 1994 (30. 08. 94)

Date of mailing of the international search report

September 13, 1994 (13. 09. 94)

Name and mailing address of the ISA/

Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP94/00920

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, A, 58-16041 (Mitsubishi Metal Corp.), January 29, 1983 (29. 01. 83), Line 5, left column to line 19, right column, page 1 & GB, A, 2,102,768	1-4